

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
23 September 2004 (23.09.2004)

PCT

(10) International Publication Number
WO 2004/081666 A1

(51) International Patent Classification⁷: **G03F 7/20**

(21) International Application Number:
PCT/US2004/003556

(22) International Filing Date: 23 January 2004 (23.01.2004)

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
10/386,356 11 March 2003 (11.03.2003) **US**

(71) Applicant (for all designated States except US): **UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL** [US/US]; 308 Bynum Hall, Campus Box 4105, Chapel Hill, NC 27599-4105 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ROLLAND, Jason,**

P. [US/US]; 108 264 Timber Hollow Court, Chapel Hill, NC 27514 (US). **DESIMONE, Joseph, M.** [US/US]; 7315 Crescent Ridge Drive, Chapel Hill, NC 27516 (US).

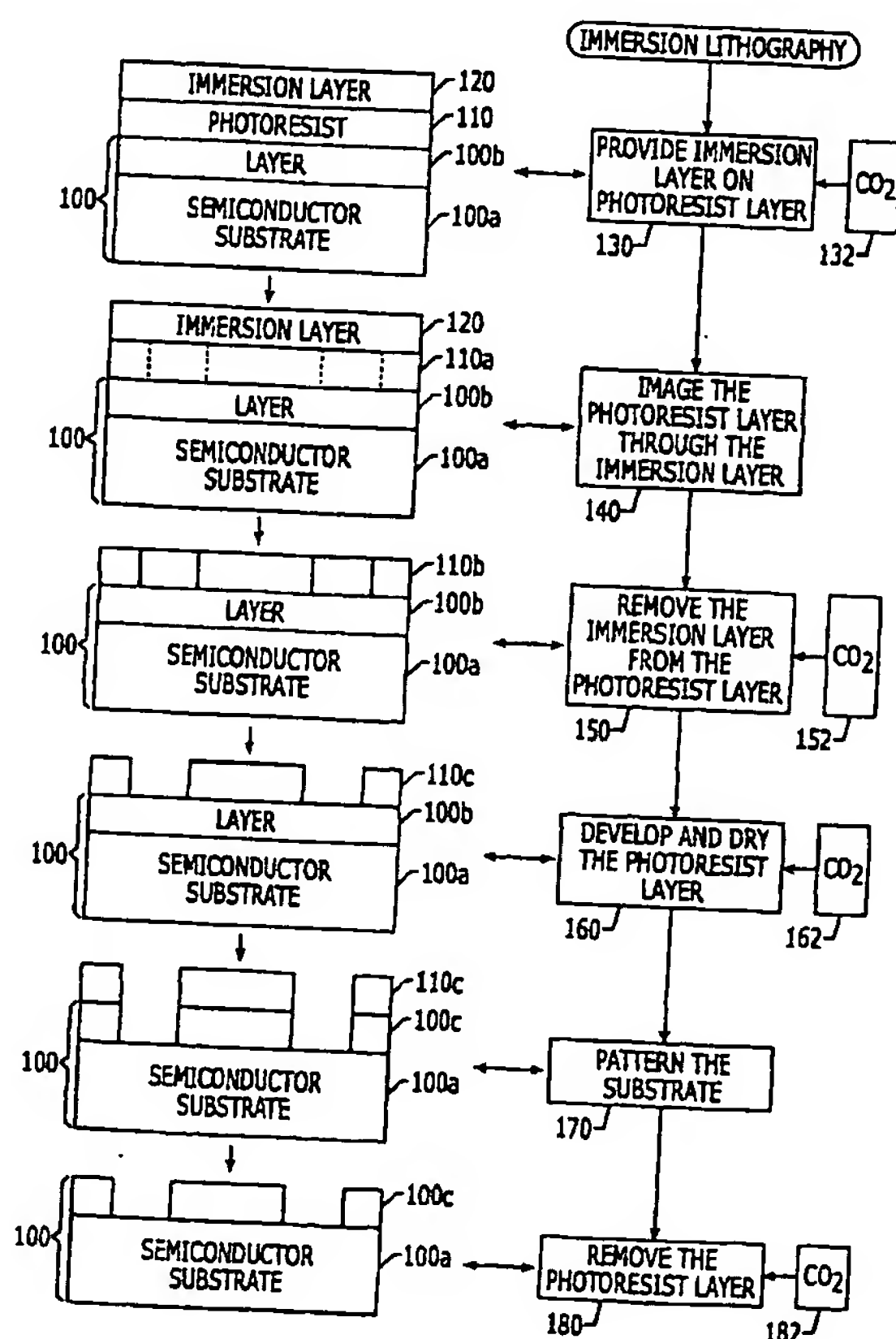
(74) Agent: **BIGEL, Mitchell, S.**; Myers Bigel Sibley & Sajovec, P.A., P.O. Box 37428, Raleigh, NC 27627 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),

[Continued on next page]

(54) Title: **IMMERSION LITHOGRAPHY METHODS USING CARBON DIOXIDE**



(57) Abstract: A substrate is patterned by performing immersion lithography on a photoresist layer on the substrate using carbon dioxide. The immersion layer may be provided and/or removed and/or the photoresist layer may be developed, dried and/or removed using carbon dioxide. The immersion layer can include liquid and/or solid immersion layers. The need for organic solvents in immersion lithography can thereby be reduced or eliminated.

WO 2004/081666 A1



Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *with international search report*

IMMERSION LITHOGRAPHY METHODS USING CARBON DIOXIDE

Field Of The Invention

The present invention relates to methods of patterning a photoresist layer on a substrate as well as methods of removing an immersion layer from a photoresist layer.

Background Of The Invention

5 To satisfy the ever-increasing desire for faster and smaller electronic devices such as personal computers, it has become desirable to increase the number of microelectronic devices such transistors on a chip without increasing the size of the chip. Accordingly, it is desirable to continually strive to reduce the size of the microelectronic devices.

10 One of the primary hurdles in achieving the much sought after size reduction of microelectronic devices is in the area of photolithography. For decades, photolithography has been utilized to pattern photoresists in the manufacture of microelectronic devices. The resolution of the image formed on a photoresist layer using photolithography generally is directly proportional to the wavelength of the radiation source (λ) and inversely proportional to the numerical aperture (NA) of the photolithography apparatus. Thus, in order to reduce
15 the feature size that can be patterned by a photolithography apparatus, it may be desirable to utilize radiation sources having shorter and shorter wavelengths and/or develop photolithography apparatus having larger numerical apertures.

Efforts have resulted in the reduction in wavelength from mercury g line (436 nm) to 193 nm using an excimer laser and further to 157 nm. Research is currently being performed
20 to further reduce the wavelength of the radiation source using x-ray lithography and/or extreme ultraviolet (EUV) lithography. The cost of continuing to reduce the wavelength of the radiation source may be enormous. New materials for photomasks and/or lenses may need to be developed. As the wavelength becomes shorter, the photolithography method may need to shift from refractive photolithography to reflective photolithography. Designing an

all-reflective camera that achieves lithographic-quality imaging may be more difficult than designing a refractive imaging system because mirrors generally have fewer degrees of freedom to vary than do lenses.

These challenges have resulted in an interesting intersection between microelectronic device manufacture and biology. When faced with the problem of increasing the resolution of microscope lenses beyond their normal magnification, biologists began placing a layer of oil between the lens and the slide to be examined. This technique, known as immersion oil microscopy, reduces the loss of image quality that would occur as a result of the difference in the refractive index between the glass of the lens and air. In an ideal situation, the refractive index of the oil is precisely matched to that of the glass so that the loss of image quality can be eliminated.

Using the principles of immersion oil microscopy, photolithographers have begun to explore an area that is coming to be known as immersion lithography. In immersion lithography, the space between the final optical element and the substrate to be patterned is at least partially filled with a high index medium. M. Switkes & M. Rothschild, "Immersion Lithography at 157 nm," J. Vac. Sci. Technol. B, 19(6): 2353-2356 (Nov/Dec 2001) proposes the use of commercially available perfluoropolyethers (PFPE's), which are widely available as oils and lubricants, for example under the trade name Fomblin® (Solvay Solexis Corp.) as the high index medium in an immersion interference lithography system. Switkes & Rothschild utilized organic solvents such as Fomblin® PFS-1 to remove them from the patterned substrate. The Switkes & Rothschild publication is hereby incorporated herein by reference in its entirety as if set forth fully herein.

Immersion lithography has been regarded as a breakthrough technology that may allow the integration density of integrated circuit devices to continue to increase without the need for post-optical next generation lithography. See, for example, the publication entitled "Liquid Immersion' could delay post-optical lithography, says MIT", by Mark LaPedus, Semiconductor Business News, March 11, 2002, and the publication entitled "What's Next: Full Immersion Lithography?" Solid State Technology, May 2002, Vol. 45, No. 5, p. 24.

Summary Of The Invention

Embodiments of the present invention provide methods of patterning a substrate by performing immersion lithography on a photoresist layer on the substrate using carbon

dioxide. It has been found, according to some embodiments of the present invention, that supercritical and/or liquid carbon dioxide may be used at various steps in an immersion lithography process and, thereby, replace the use of some or all solvents that have been heretofore been used to deposit the immersion fluid, to remove the immersion fluid and/or to
5 perform various other steps in immersion lithography. The use of organic solvents in immersion photolithography may have a large environmental and/or economic impact on the immersion lithography process. In contrast, embodiments of the invention can reduce or eliminate the need for such organic solvents.

In some embodiments of the present invention, immersion lithography is performed
10 on a photoresist layer on a substrate by providing an immersion layer on the photoresist layer, imaging the photoresist layer through the immersion layer, removing the immersion layer from the photoresist layer, developing the photoresist layer from which the immersion layer has been removed, drying the photoresist layer from which the immersion layer has been removed, patterning the substrate using the photoresist layer that has been developed and
15 removing the photoresist layer from the substrate that has been patterned. According to embodiments of the present invention, one or more of the steps of providing an immersion layer, removing the immersion layer, developing the photoresist layer, drying the photoresist layer and removing the photoresist layer is performed using carbon dioxide.

In some embodiments, carbon dioxide is used in providing an immersion layer on the
20 photoresist layer. In some embodiments, a fluid layer is deposited onto the photoresist layer, wherein the fluid layer comprises carbon dioxide and at least one immersion compound. At least some of the carbon dioxide is then removed from the fluid layer to provide an immersion fluid layer on the photoresist layer.

In other embodiments, carbon dioxide is used to remove an immersion layer from a
25 photoresist layer. In some of these embodiments, an immersion layer is formed on the photoresist layer and the photoresist layer is imaged through the immersion layer. The immersion layer is removed from the imaged photoresist by contacting the immersion layer with an immersion rinse composition that comprises liquid and/or supercritical carbon dioxide.

30 In still other embodiments, carbon dioxide is used to dry a photoresist layer. In some embodiments, an immersion layer is formed on the photoresist layer, the photoresist layer is imaged through the immersion layer and the immersion layer is removed from the photoresist

layer. The photoresist layer from which the immersion layer has been removed is dried using liquid and/or supercritical carbon dioxide.

In yet other embodiments, carbon dioxide is used to develop the photoresist layer. In particular, in some embodiments, an immersion layer is formed on the photoresist layer, the photoresist layer is imaged through the immersion layer and the immersion layer is removed from the photoresist layer. The photoresist layer from which the immersion layer has been removed is developed using liquid and/or supercritical carbon dioxide. In other embodiments, the immersion layer is removed from the photoresist layer and the photoresist layer is simultaneously developed using liquid and/or supercritical carbon dioxide.

In still other embodiments of the present invention, carbon dioxide is used to remove the photoresist layer and/or clean the substrate after the substrate has been patterned. In particular, in some embodiments, an immersion layer is formed on the photoresist layer, the photoresist layer is imaged through the immersion layer and the immersion layer is removed from the photoresist layer. The photoresist layer from which the immersion layer has been removed is developed and the substrate is patterned using the photoresist layer that has been developed. The photoresist layer is then removed from the substrate that has been patterned using liquid and/or supercritical carbon dioxide.

In still other embodiments, a solid immersion film is placed on (contacted to) the photoresist layer and the photoresist layer is imaged through the solid immersion film. In some embodiments, the solid immersion film includes carbon dioxide and at least one solid immersion film compound. However, in other embodiments, the solid immersion film need not comprise carbon dioxide. Moreover, in still other embodiments, an immersion fluid layer is first formed on the photoresist layer and the solid immersion film is then placed on the immersion fluid layer opposite the photoresist layer. The immersion fluid layer between the solid immersion film and the photoresist layer can improve the contact between the solid immersion film and the photoresist layer. The immersion fluid layer may include carbon dioxide in some embodiments, but need not include carbon dioxide in other embodiments. Thus, some embodiments of the present invention provide the use of solid immersion films, also referred to herein as contact immersion films, in immersion lithography, with or without an intervening immersion fluid layer.

Brief Description of the Drawings

Figure 1 is a flowchart of methods of patterning a substrate according to various embodiments of the present invention, and includes cross-sectional views of substrates that are patterned according to various embodiments of the present invention corresponding to blocks of the flowchart.

Figures 2A-2B are cross-sectional views of substrates that are patterned according to other embodiments of the present invention.

Figures 3A-3B are cross-sectional views of substrates that are patterned according to yet other embodiments of the present invention.

Figure 4 illustrates an immersion interference lithography apparatus that can be employed in performing methods according to embodiments of the present invention; and

Figure 5 illustrates a semiconductor processing apparatus that can be employed in performing methods according to embodiments of the present invention.

Detailed Description Of Preferred Embodiments

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which embodiments of the invention are shown. However, this invention should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, the thickness of layers and regions are exaggerated for clarity. Like numbers refer to like elements throughout. It will be understood that when an element such as a layer, region or substrate is referred to as being "on" or extending "onto" another element, it can be directly on or extend directly onto the other element or intervening elements may also be present. In contrast, when an element is referred to as being "directly on" or extending "directly onto" another element, there are no intervening elements present.

Figure 1 is a flowchart of methods of patterning a substrate according to embodiments of the present invention, and includes cross-sectional views of substrates that are patterned according to various embodiments of the present invention corresponding to blocks of the flowchart. Referring now to Figure 1, a substrate is patterned according to embodiments of the present invention by performing immersion lithography on a photoresist layer on a substrate using carbon dioxide. As shown in Figure 1, the substrate 100 may

comprise a semiconductor substrate 100a and may also include one or more layers 100b on the semiconductor substrate 100a. As is well known to those having skill in the art, the semiconductor substrate 100a may include a monocrystalline, single element and/or compound semiconductor substrate and/or a monocrystalline, single element and/or compound semiconductor layer, such as an epitaxial layer, thereon. The layer 100b may include one or more insulating layers such as silicon dioxide, silicon nitride and/or other conventional insulating layers, one or more conductive layers, such as a metal and/or doped polysilicon layer and/or any other conventional layer that is used microelectronic device manufacturing. In order to pattern the substrate 100 including patterning the semiconductor substrate 100a and/or patterning a layer 100b, a photoresist layer 110 is provided on a substrate 100, using conventional techniques.

Referring to Block 130, an immersion layer 120, also referred to herein as an immersion fluid layer, is provided on the photoresist layer 110. In some embodiments of the invention, the immersion layer 120 is provided using carbon dioxide 132 by depositing a fluid layer onto the photoresist layer 110, the fluid layer comprising carbon dioxide and at least one immersion compound. At least some of the carbon dioxide is then removed from the fluid layer to provide an immersion fluid layer 120 on the photoresist layer 110. In some embodiments, the fluid layer comprises liquid and/or supercritical carbon dioxide. In other embodiments, the at least one immersion fluid compound comprises a fluorine and/or silicon containing compound such as a perfluoropolyether compound. In other embodiments, the at least one immersion fluid compound comprises a polymer. Many examples will be provided below.

Referring again to Figure 1, at Block 140, the photoresist layer is imaged through the immersion layer to produce an imaged photoresist layer 110a. Imaging may be performed using known immersion lithography processes, such as described in the above-cited Switkes & Rothschild publication. Then, at Block 150, the immersion layer 120 is removed from the imaged photoresist layer 110a. In some embodiments, CO₂ 152 is used during the process of removing the immersion layer 120 from the imaged photoresist layer 110a at Block 150. In particular, in some embodiments, the immersion layer is contacted with an immersion rinse composition comprising liquid and/or supercritical carbon dioxide as will be described in detail below.

Referring again to Figure 1, at Block 160, the photoresist layer 110b is developed and dried to produce a patterned photoresist layer 110c. In some embodiments, CO₂ 162 is used during the process of developing and/or drying the photoresist layer. In particular, in some embodiments, the photoresist layer from which the immersion layer has been removed is
5 dried using liquid and/or supercritical carbon dioxide. In still other embodiments, the photoresist layer from which the immersion layer has been removed is developed using liquid and/or supercritical carbon dioxide 162. In yet other embodiments, carbon dioxide is used to develop and dry the photoresist layer. In still other embodiments, carbon dioxide is used to simultaneously develop and dry the photoresist layer. Techniques for drying and/or
10 developing photoresist using carbon dioxide are known to those having skill in the art and need not be described further herein.

Referring again to Figure 1, at Block 170, the substrate is patterned using conventional patterning techniques such as wet and/or dry etching. A patterned layer 100c is thereby produced. Then, at Block 180, the patterned photoresist layer 110c is removed. In
15 some embodiments of the invention, liquid and/or supercritical carbon dioxide is used to remove the patterned photoresist layer 110c from the substrate 100. Techniques for removing photoresist using carbon dioxide are known to those having skill in the art and need not be described further herein.

Figures 2A-2B are cross-sectional views illustrating other embodiments of providing
20 an immersion layer on a photoresist layer (Block 130 of Figure 1) according to the present invention. As shown in Figure 2A, a solid immersion film 220 is placed on (contacted to) the photoresist layer 110 to form a solid immersion film, as shown in Figure 2B. The composition of the solid immersion film 220 will be described below. The solid immersion film 220 may be attached using standard techniques for placing a solid thin film on a
25 substrate. In some embodiments, the solid immersion film 220 comprises carbon dioxide and at least one solid immersion film compound. Then, as was described above in connection with Block 130, the carbon dioxide is removed from the solid immersion film. In other embodiments, a solid immersion film may be used to pattern a substrate in an immersion lithography process without using CO₂. Accordingly, solid immersion lithography may be
30 provided, with or without using carbon dioxide in the process.

Figures 3A-3B are cross-sectional views of immersion lithography processes according to yet other embodiments of the present invention. In these embodiments, an

immersion fluid layer 330 is interposed between the solid immersion film 320, which may be similar to the solid immersion film 220 of Figure 2A, and the photoresist 110, to promote enhanced contact and/or a more uniform optical interface between the solid immersion film 320 and the photoresist 110. Figure 3B illustrates a solid immersion film 320 on the photoresist 110 with an immersion fluid layer 330 therebetween. In some embodiments, the solid immersion film 320 is substantially thicker than the immersion fluid layer 320, so that the immersion lithography parameters are governed primarily by the solid immersion film 320. In other embodiments, differing thickness ratios may be used. In still other embodiments, the use of a solid immersion film 320 and a liquid immersion layer 330 may be used in immersion lithography processes that do not involve CO₂. It will be understood that conventional immersion lithography and/or immersion lithography of Figure 1 may then be performed on embodiments of Figures 2B and/or 3B.

Additional discussion of various embodiments of the present invention now will be described.

According to some embodiments of the present invention, a method of patterning a photoresist layer on a substrate includes depositing a fluid layer, which includes carbon dioxide and at least one immersion compound, onto the photoresist layer and removing the carbon dioxide from the fluid layer to provide an immersion fluid layer on the photoresist layer.

The fluid layer may be deposited on the photoresist layer by various processes as will be understood by those skilled in the art. For example, in some embodiments, the immersion fluid is spin coated on the substrate. In other embodiments, the immersion fluid dissolved in a solvent is spin coated on the substrate, wherein the solvent comprises CO₂. In other embodiments, a free meniscus coating method such as dip coating and/or knife coating may be used.

The carbon dioxide may be in a liquid, gaseous, or supercritical phase. If liquid CO₂ is used, the temperature employed during the process is below 31°C in some embodiments. If gaseous CO₂ is used, the phase may be employed at high pressure. As used herein, the term "high pressure" generally refers to CO₂ having a pressure from about 50 to about 500 bar. In some embodiments, the CO₂ is utilized in a "supercritical" phase. As used herein, "supercritical" means that a fluid medium is above its critical temperature and pressure, i.e., about 31°C and about 71 bar for CO₂. The thermodynamic properties of CO₂ are reported in

Hyatt, *J. Org. Chem.* 49: 5097-5101 (1984); therein, it is stated that the critical temperature of CO₂ is about 31°C; thus in some embodiments of the present invention may be carried out at a temperature above 31°C. For the purposes of the invention, CO₂ at a pressure ranging from at a lower end of about 20 or about 50 bar to an upper end of about 200 bar or about 1000 bar
5 may be employed.

The immersion fluid compound may be selected from various immersion fluid compounds including, but not limited to, perfluoropolyethers and other suitable fluorinated compounds. Other suitable fluorinated compounds may include fluoroalkyl (meth)acrylate homo- and copolymers, homo- and copolymers of tetrafluoroethylene, hexafluoropropylene,
10 perfluorodimethyldioxole, norbornene, vinylidene fluoride and norbornene derivatives, as described for example in published International Patent Application Nos. WO 00/17712 and WO 00/67072. The material also may contain silicon or siloxane units such as polydimethylsiloxane or polydialkylsilanes. These materials may be CO₂ soluble, so that they can be soluble deposited in CO₂. In general, the immersion fluid compound should be
15 transparent enough to allow a working distance between a final optical element and a microelectronic workpiece of at least 10 µm. The immersion fluid compound should not interact with the photoresist such that it would impede image formation. In addition, the immersion fluid compound should be compatible with the clean room environment and the semiconductor manufacturing process. In some embodiments, the immersion fluid
20 compound is nontoxic and/or is chemically inert.

In other embodiments, the immersion fluid may also take the form of a contact film of a high transparency material that may be derived from the materials listed above, including a crosslinked material such as a crosslinked PFPE film. In still other embodiments, the immersion fluid may take the form of a contact film as described above, and an interposed
25 liquid immersion layer of the type described above.

In some embodiments, the immersion fluid compound is resistant to damage by radiation (e.g., lasers) from sources that are used for photolithography. The resistance of the immersion fluid compound to damage by radiation sources can be determined by measuring the change in transmission for the compound following exposure to the radiation source of
30 interest. For example, a layer of the immersion fluid compound can be placed between two CaF₂ windows and irradiated at 157 nm using a standard dose, such as 100 J/cm at a fluence of 0.3 mJ/cm²-pulse and the change in transmission measured for the compound. In some

embodiments, particularly those in which the immersion fluid compound is to be used for multiple exposures, the change in transmission may be less than 50 percent and in other embodiments may be less than 25 percent. While the immersion fluid compound is preferably resistant to damage by the radiation source of interest, immersion fluid compounds of the present invention may still be utilized if they are easily damaged by the radiation source of interest. In these cases, the immersion fluid compound can be replaced after 1, 2, 3, 4, or 5 exposures. For example, an immersion fluid compound that is easily damaged by the radiation source of interest could travel with the wafer, providing fresh immersion fluid compound for each exposed field.

10 The carbon dioxide can be removed from the fluid layer to provide the immersion fluid layer by various processes as will be understood by those skilled in the art including, but not limited to, reducing the pressure of the fluid layer and/or increasing the temperature of the fluid layer. Because the microelectronic workpiece typically has a thermal budget, it may be desirable in some embodiments to remove the carbon dioxide from the fluid layer by
15 reducing the pressure of the fluid layer.

In some embodiments, the refractive index of the immersion fluid layer should be within 10 to 20 percent of the refractive index for the optics of the imaging apparatus. For example, if CaF_2 optics ($n = 1.56$, where n is the refractive index) are used in the imaging apparatus, the immersion fluid compound can have a refractive index between a lower limit
20 of 1.25 or 1.40 and an upper limit of 1.72 or 1.87.

In some embodiments, methods of patterning a photoresist layer according to the present invention include placing the substrate having a photoresist layer thereon into a carbon dioxide chamber prior to the depositing of the immersion fluid layer. The carbon dioxide chamber is a chamber that can withstand the pressures and temperatures for
25 processing with liquid or supercritical carbon dioxide, as described above. The carbon dioxide chamber may be on a track. As is well known to those having skill in the art, microelectronic devices may be fabricated using an ensemble of tools on a track. A CO_2 chamber can be added to the track to perform immersion lithography according to some embodiments of the present invention.

30 In some embodiments, the carbon dioxide chamber is a part of a microelectronic device processing apparatus, such as the one illustrated in Figure 5. The apparatus includes a loadlock chamber 510 having a cassette 520 loaded with one or more semiconductor wafers

530 (a semiconductor substrate). The loadlock chamber 510 is connected to a transfer chamber 560. The transfer chamber 560 may be used to transfer the semiconductor wafer 530 from a first chamber within the apparatus to a second chamber within the apparatus. While the transfer chamber 560 as illustrated in Figure 5 has robot arms 550 for loading and unloading the semiconductor wafer 530, it is to be understood that various means for loading and unloading the semiconductor wafer 530 may be used. As shown in Figure 5, the transfer chamber 560 is connected to a carbon dioxide chamber 540.

In some embodiments of the present invention, a method of patterning a photoresist layer includes contacting the immersion fluid layer with an immersion rinse composition (Block 150 of Figure 1). The contacting of the immersion fluid layer with the immersion rinse composition may be performed by various processes as will be understood by those in the art including, but not limited to, rinsing with a solvent such as CFCs, HCFCs, HFCs and FCs, or a non-molecular etchant, PFP solvent or fluoroether. In some embodiments, the contacting of the immersion fluid layer with an immersion rinse composition is performed in a carbon dioxide chamber. The carbon dioxide chamber is a chamber that can withstand the pressures and temperatures for processing with liquid or supercritical carbon dioxide, as described above. In some embodiments, the carbon dioxide chamber is on a track. When a carbon dioxide chamber is used for depositing the immersion fluid layer and a carbon dioxide chamber is used for removing the immersion fluid layer, the carbon dioxide chamber utilized for the depositing the immersion fluid layer may be the same carbon dioxide chamber utilized for removal of the immersion fluid layer or may be a different carbon dioxide chamber.

The immersion rinse composition is a composition capable of removing all or substantially all of the immersion fluid layer from the patterned photoresist layer. The immersion rinse composition may be an aqueous composition, an organic composition, or a carbon-dioxide based (e.g., comprising greater than 50 percent carbon dioxide) composition. The immersion rinse composition comprises liquid or supercritical carbon dioxide in some embodiments, as described above.

In some embodiments, the immersion rinse composition comprises liquid or supercritical carbon dioxide and a co-solvent. Exemplary co-solvents that could be used include, but are not limited to, alcohols (e.g., methanol, ethanol, and isopropanol); fluorinated and other halogenated solvents (e.g., chlorotrifluoromethane, trichlorofluoromethane, perfluoropropane, chlorodifluoromethane, and sulfur hexafluoride); amines (e.g., N-methyl

pyrrolidone); amides (e.g., dimethyl acetamide); aromatic solvents (e.g., benzene, toluene, and xylenes); esters (e.g., ethyl acetate, dibasic esters, and lactate esters); ethers (e.g., diethyl ether, tetrahydrofuran, and glycol ethers); aliphatic hydrocarbons (e.g., methane, ethane, propane, ammonium butane, n-pentane, and hexanes); oxides (e.g., nitrous oxide); olefins
5 (e.g., ethylene and propylene); natural hydrocarbons (e.g., isoprenes, terpenes, and d-limonene); ketones (e.g., acetone and methyl ethyl ketone); organosilicones; alkyl pyrrolidones (e.g., N-methyl pyrrolidone); paraffins (e.g., isoparaffin); petroleum-based solvents and solvent mixtures; and any other compatible solvent or mixture that is available and suitable. Mixtures of the above co-solvents may be used.

10 According to still other embodiments of the present invention, a method of patterning a photoresist layer on a substrate includes depositing an immersion fluid layer onto the photoresist layer, imaging the photoresist layer to provide an imaged photoresist layer, and contacting the immersion fluid layer with an immersion rinse composition, which includes liquid or supercritical carbon dioxide, to remove the immersion fluid layer from the imaged
15 photoresist layer.

The immersion fluid layer may be deposited on the photoresist layer as described above at Block 130. The immersion fluid layer may include various immersion fluid compounds including, but not limited to, perfluoropolyethers. In some embodiments, the immersion fluid layer is Fomblin[®] Y (e.g., Fomblin[®] Y-18 or Fomblin[®] Y-140) or Fomblin[®]
20 Z (e.g., Fomblin[®] Z-25) commercially available from Solvay Solexis of Thorofare, New Jersey. In other embodiments, the immersion fluid layer is a perfluoropolyether or other suitable fluorinated compound layer that has been deposited utilizing carbon dioxide as described above. The immersion fluid compound and/or immersion fluid layer may have similar characteristics to one or more of the various characteristics described above with
25 respect to immersion fluid compounds and immersion fluid layers such as transparency, freedom from optical defects, minimal or no interaction with the resist to impede image formation, compatibility with the clean room environment and the semiconductor manufacturing process, not toxic, chemically inert, resistant to damage by the radiation of interest, and/or index matched with the final optical element.

30 After depositing the immersion fluid layer, the photoresist layer may be imaged utilizing various immersion lithography processes (Block 140). In general, "dry" (i.e., non-immersion) lithography apparatus can be converted to immersion lithography processes by,

for example, introducing a layer of immersion fluid between, for example, the final optical element and the photoresist layer on the semiconductor substrate. For example, as illustrated in Figure 4, an interference lithography system 400 will now be described. The interference lithography system 400 may be a conventional interference lithography system as will be understood by those skilled in the art with the exception that an immersion fluid layer 460 has been deposited between the final optical element 450 and the microelectronic workpiece 470, which comprises a substrate with a photoresist layer thereon, where the photoresist layer is adjacent the immersion fluid layer. In general, a radiation source 410 such as a Lambda-Physik LPX-200 F₂ laser emits a laser beam 420. The laser beam 420 is split into two polarized arms by partial reflection from the reflecting plates 430, which may comprise, for example, CaF₂. The arms are then reflected in the mirrors 440, which may comprise, for example, Si, and eventually enter the final optical element 450. The arms then pass through the immersion fluid layer 460 and intersect at the surface of the microelectronic workpiece 470. While embodiments of the present invention have been described with reference to an interference lithography system, it is to be understood that the present invention may be performed utilizing various lithography systems as will be understood by those skilled in the art including, but not limited to, projection lithography and/or contact printing lithography.

After imaging the photoresist layer, the immersion layer is removed (Block 160) by contacting the immersion layer with an immersion rinse composition as described above.

According to other embodiments of the present invention, a method of removing an immersion fluid layer from an imaged photoresist layer on a substrate includes contacting the immersion fluid layer with an immersion rinse composition comprising liquid or supercritical carbon dioxide to remove the immersion fluid layer from the imaged photoresist layer. The contacting operation, immersion fluid layer, and immersion rinse composition can be similar to those described above.

In still other embodiments, as was described above, an immersion fluid is deposited, the photoresist is imaged and the immersion fluid is rinsed off. The photoresist is developed, for example, using TMAH and/or other conventional developer. Then, the patterned photoresist is dried using CO₂ and/or CO₂ with surfactants. By using CO₂ and/or CO₂ with surfactants, image collapse can be reduced or prevented. In still other embodiments, development may take place directly using CO₂ for negative or positive tone images using techniques that are known to those having skill in the art.

In still other embodiments, non-CO₂ methods may be used for applying and removing the immersion fluid, but then CO₂ may be used to assist in developing the pattern in the resist, either using CO₂ directly to develop the pattern or using standard development methods followed by CO₂-based drying methods. CO₂ may be used to simultaneously
5 develop the photoresist layer and remove the immersion layer in other embodiments. In still other embodiments, as was described above, the photoresist is cleaned or removed using carbon dioxide.

In still other embodiments, the immersion fluid is a polymeric film and is physically placed onto the photoresist, with or without using carbon dioxide. In still other embodiments,
10 a liquid is placed between the polymeric film and the photoresist with or without the use of carbon dioxide.

In the specification, there has been disclosed embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following
15 claims.

That Which is Claimed is:

1. A method of patterning a substrate comprising:
performing immersion lithography on a photoresist layer on the substrate using carbon dioxide.
2. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on the substrate using carbon dioxide comprises:
providing an immersion layer on the photoresist layer;
imaging the photoresist layer through the immersion layer;
removing the immersion layer from the photoresist layer;
developing the photoresist layer from which the immersion layer has been removed;
drying the photoresist layer from which the immersion layer has been removed;
patterning the substrate using the photoresist layer that has been developed; and
removing the photoresist layer from the substrate that has been patterned;
wherein one or more of the providing an immersion layer, removing the immersion layer, developing the photoresist layer, drying the photoresist layer and removing the photoresist layer is performed using carbon dioxide.
3. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on the substrate using carbon dioxide comprises:
depositing a fluid layer onto the photoresist layer, the fluid layer comprising carbon dioxide and at least one immersion compound; and
removing at least some of the carbon dioxide from the fluid layer to provide an immersion fluid layer on the photoresist layer.
4. A method according to Claim 3 wherein the fluid layer comprises liquid and/or supercritical carbon dioxide.
5. A method according to Claim 3 wherein the at least one immersion fluid compound comprises a fluorine and/or silicon-containing compound.

6. A method according to Claim 5 wherein the fluorine and/or silicon-containing compound comprises a perfluoropolyether compound.
7. A method according to Claim 3 wherein the at least one immersion fluid compound comprises a polymer.
8. A method according to Claim 3 wherein the depositing a fluid layer is performed in a carbon dioxide chamber.
9. A method according to Claim 8 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.
10. A method according to Claim 2 wherein the drying is performed prior to the developing.
11. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:
 - forming an immersion layer on the photoresist layer;
 - imaging the photoresist layer through the immersion layer; and
 - removing the immersion layer from the imaged photoresist layer by contacting the immersion layer with an immersion rinse composition comprising liquid and/or supercritical carbon dioxide.
12. A method according to Claim 11 wherein the forming an immersion layer comprises:
 - depositing a fluid layer onto the photoresist layer, the fluid layer comprising carbon dioxide and at least one immersion fluid compound; and
 - removing the carbon dioxide from the fluid layer to provide the immersion layer on the photoresist layer.
13. A method according to Claim 12 wherein the fluid layer comprises liquid and/or supercritical carbon dioxide.

14. A method according to Claim 12 wherein the at least one immersion fluid compound comprises a fluorine and/or silicon-containing compound.
15. A method according to Claim 14 wherein the fluorine and/or silicon-containing compound comprises a perfluoropolyether compound.
16. A method according to Claim 12 wherein the at least one immersion fluid compound comprises a polymer.
17. A method according to Claim 12 wherein the depositing a fluid layer is performed in a carbon dioxide chamber.
18. A method according to Claim 17 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.
19. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:
 - forming an immersion layer on the photoresist layer;
 - imaging the photoresist layer through the immersion layer;
 - removing the immersion layer from the photoresist layer; and
 - drying the photoresist layer from which the immersion layer has been removed using liquid and/or supercritical carbon dioxide.
20. A method according to Claim 19 wherein the drying is performed in a carbon dioxide chamber.
21. A method according to Claim 20 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.
22. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:

forming an immersion layer on the photoresist layer;
imaging the photoresist layer through the immersion layer;
removing the immersion layer from the photoresist layer; and
developing the photoresist layer from which the immersion layer has been removed
using liquid and/or supercritical carbon dioxide.

23. A method according to Claim 22 wherein the developing is performed in a carbon dioxide chamber.

24. A method according to Claim 23 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

25. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:
forming an immersion layer on the photoresist layer;
imaging the photoresist layer through the immersion layer; and
removing the immersion layer from the photoresist layer and simultaneously developing the photoresist layer using liquid and/or supercritical carbon dioxide.

26. A method according to Claim 25 wherein the removing and simultaneously developing is performed in a carbon dioxide chamber.

27. A method according to Claim 8 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

28. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:
forming an immersion layer on the photoresist layer;
imaging the photoresist layer through the immersion layer;
removing the immersion layer from the photoresist layer;
developing the photoresist layer from which the immersion layer has been removed;
patterning the substrate using the photoresist layer that has been developed; and

removing the photoresist layer from the substrate that has been patterned using liquid and/or supercritical carbon dioxide.

29. A method according to Claim 28 wherein the removing is performed in a carbon dioxide chamber.

30. A method according to Claim 26 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

31. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:
placing a solid immersion film on the photoresist layer; and
imaging the photoresist layer through the solid immersion film.

32. A method according to Claim 31 wherein the placing a solid immersion film on the photoresist layer comprises:
placing a solid immersion film comprising carbon dioxide and at least one solid immersion film compound on the photoresist layer; and
removing the carbon dioxide from the solid immersion film.

33. A method according to Claim 31 wherein the placing a solid immersion film on the photoresist layer is preceded by placing an immersion fluid layer on the photoresist layer and wherein the placing a solid immersion film on the photoresist layer comprises placing a solid immersion film on the immersion fluid layer opposite the photoresist layer.

34. A method according to Claim 33 wherein the placing an immersion fluid layer comprises:
depositing a fluid layer onto the photoresist layer, the fluid layer comprising carbon dioxide and at least one immersion compound; and
removing at least some of the carbon dioxide from the fluid layer to provide an immersion fluid layer on the photoresist layer.

35. A method according to Claim 34 wherein the fluid layer comprises liquid and/or supercritical carbon dioxide.
36. A method according to Claim 34 wherein the at least one immersion fluid compound comprises a fluorine and/or silicon-containing compound.
37. A method according to Claim 36 wherein the fluorine and/or silicon-containing compound comprises a perfluoropolyether compound.
38. A method according to Claim 34 wherein the at least one immersion fluid compound comprises a polymer.
39. A method according to Claim 34 wherein the depositing a fluid layer is performed in a carbon dioxide chamber.
40. A method according to Claim 39 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.
41. A method of patterning a substrate comprising:
placing a solid immersion film on a photoresist layer on a substrate; and
imaging the photoresist layer through the solid immersion film that was placed on the photoresist layer.
42. A method according to Claim 71 wherein the placing a solid immersion film on the photoresist layer is preceded by placing a liquid immersion layer on the photoresist layer and wherein the placing a solid immersion film on the photoresist layer comprises placing a solid immersion film on the liquid immersion layer opposite the photoresist layer.
43. A method according to Claim 42 wherein the placing an immersion fluid layer comprises:
depositing a fluid layer onto the photoresist layer, the fluid layer comprising carbon dioxide and at least one immersion compound; and

removing at least some of the carbon dioxide from the fluid layer to provide an immersion fluid layer on the photoresist layer.

44. A method according to Claim 43 wherein the fluid layer comprises liquid and/or supercritical carbon dioxide.

45. A method according to Claim 43 wherein the at least one immersion fluid compound comprises a fluorine and/or silicon-containing compound.

46. A method according to Claim 45 wherein the fluorine and/or silicon-containing compound comprises a perfluoropolyether compound.

47. A method according to Claim 43 wherein the at least one immersion fluid compound comprises a polymer.

48. A method according to Claim 43 wherein the depositing a fluid layer is performed in a carbon dioxide chamber.

49. A method according to Claim 48 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

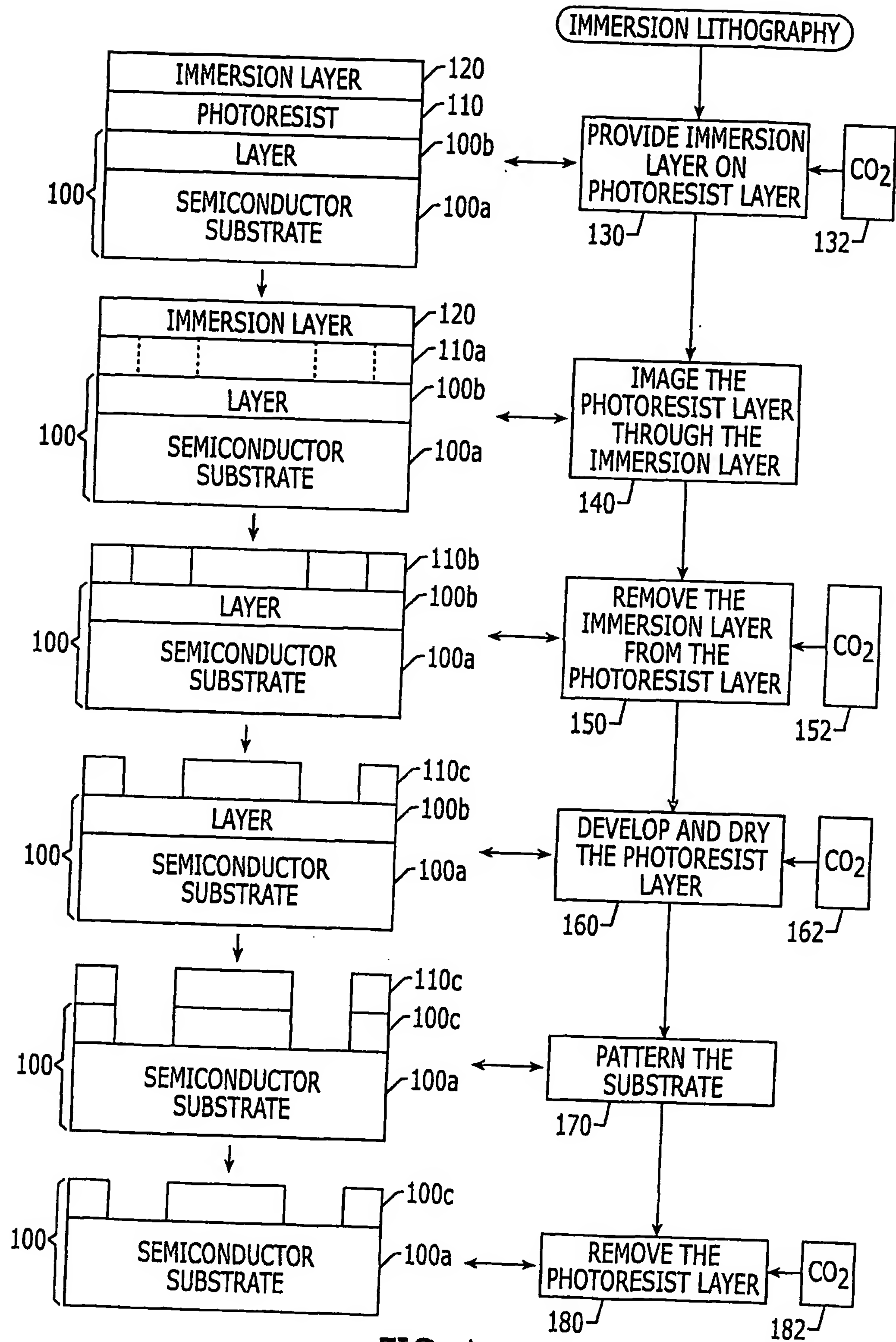


FIG. 1

2/3

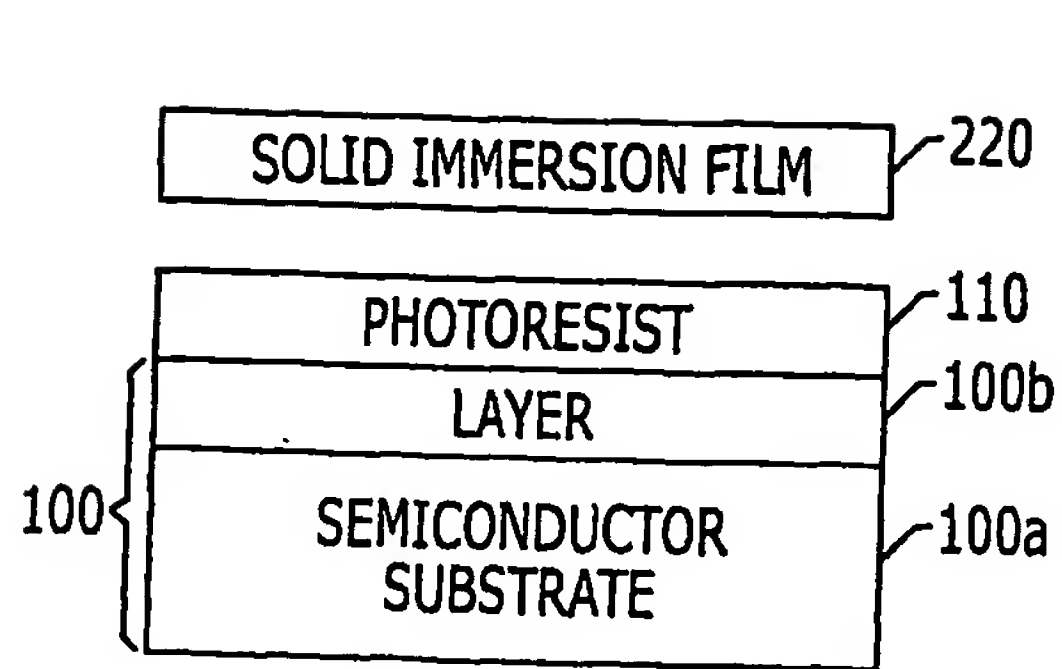


FIG. 2A

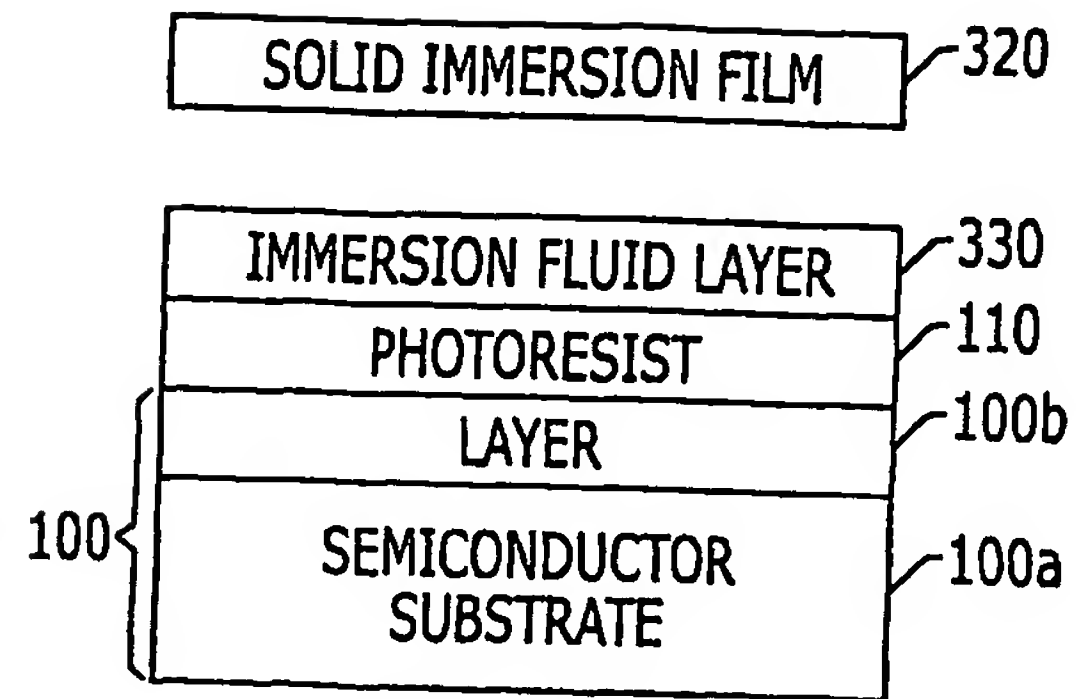


FIG. 3A

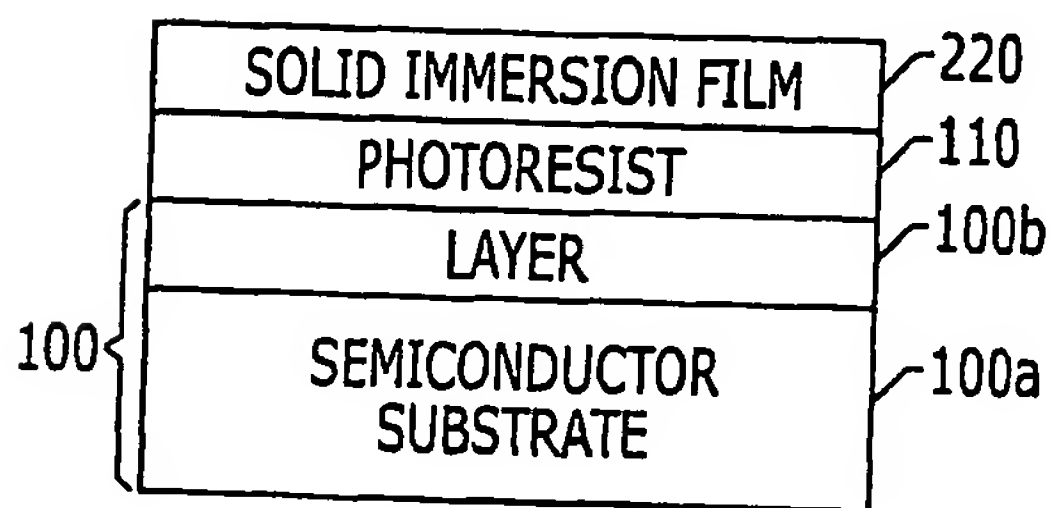


FIG. 2B

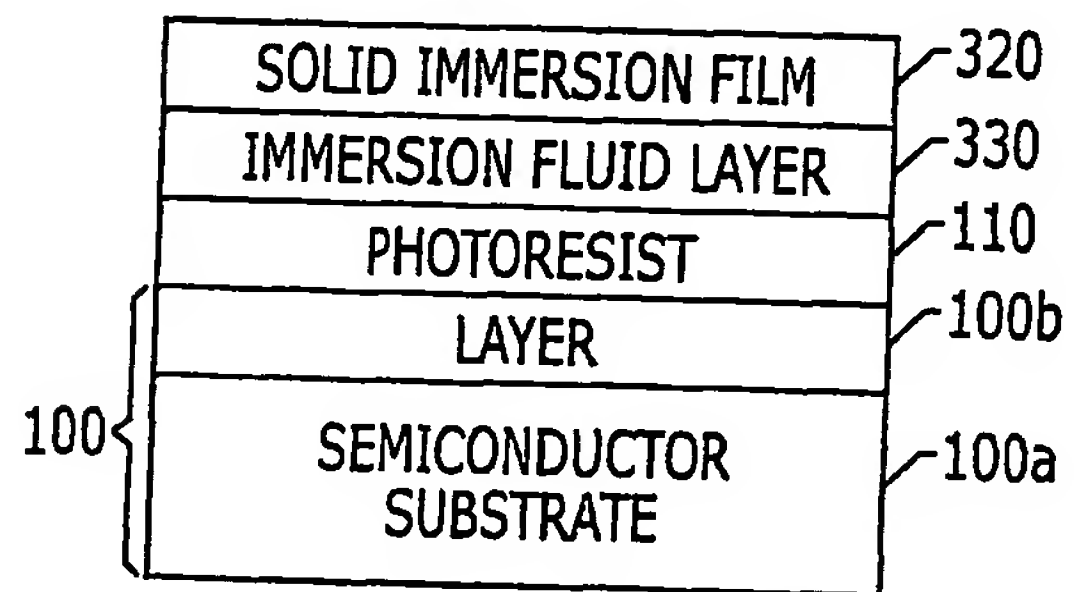


FIG. 3B

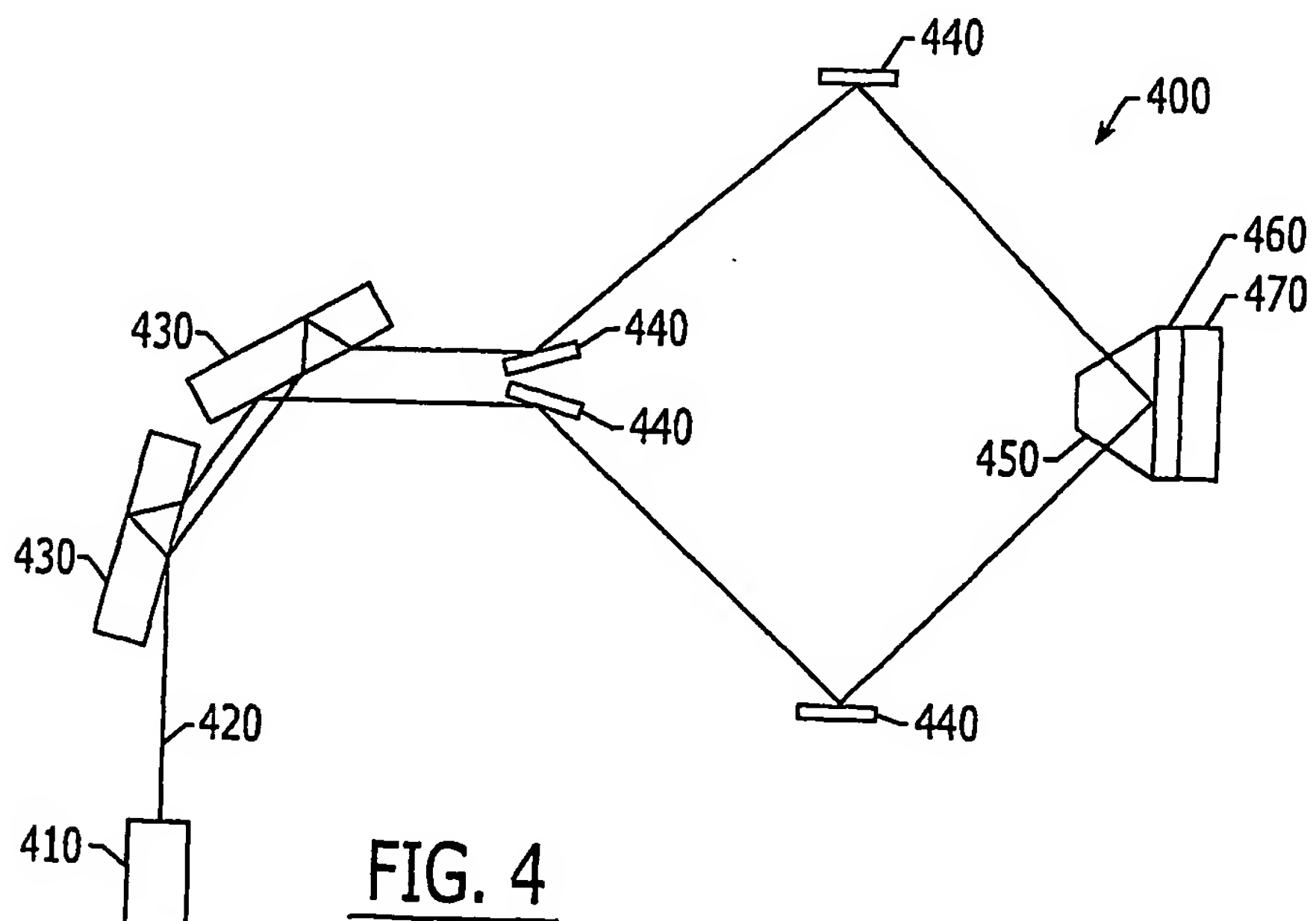
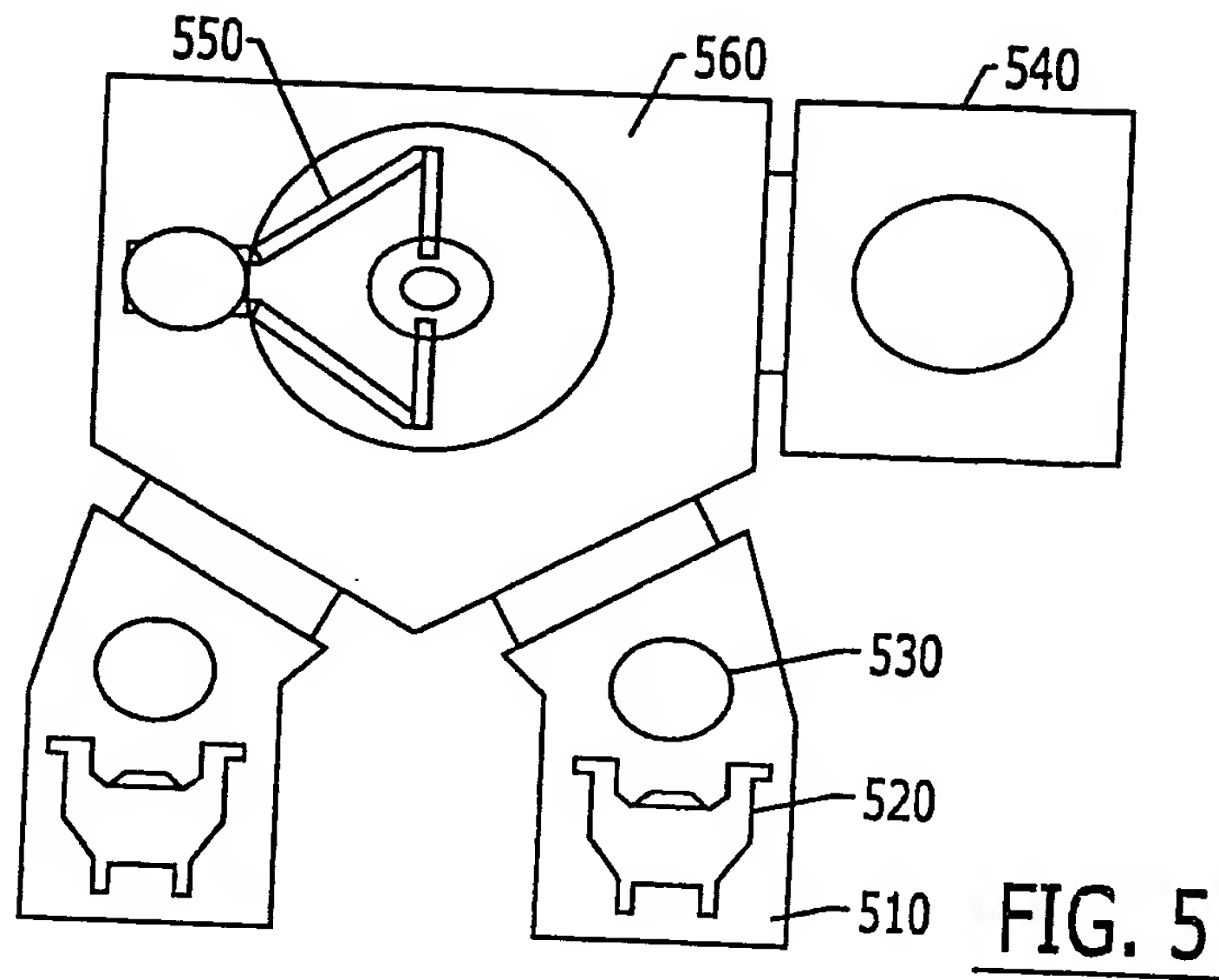


FIG. 4

3/3



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/003556

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/01797 A (BATCHELDER JOHN SAMUEL) 14 January 1999 (1999-01-14) page 1, lines 10-25; claims 1,15,17,18; table 1 page 4, lines 15-25 page 9, lines 1-3 page 9, line 9 - page 10, line 22	1-49
X	M. SWITKES, R. R. KUNZ, R. F. SINTA, M. ROTHSCHILD: "Immersion Liquids for Lithography in the Deep Ultraviolet" PROCEED. OF SPIE, vol. 5040, 25 February 2003 (2003-02-25), pages 690-699, XP002285465 abstract; figure 8 page 693, lines 28-46	1-49
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents:**

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

22 June 2004

Date of mailing of the international search report

05/07/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Thiele, N

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/003556

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/163629 A1 (SWITKES MICHAEL ET AL) 7 November 2002 (2002-11-07) claims 15,16	1-49
Y	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 06, 22 September 2000 (2000-09-22) & JP 2000 085025 A (NIKON CORP), 28 March 2000 (2000-03-28) abstract	1-49
A	SWITKES M ET AL: "RESOLUTION ENHANCEMENT OF 157 NM LITHOGRAPHY BY LIQUID IMMERSION" PROCEEDINGS OF THE SPIE, SPIE, BELLINGHAM, VA, US, vol. 4691, 5 March 2002 (2002-03-05), pages 459-465, XP009014679 ISSN: 0277-786X abstract	1-49

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/003556

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9901797	A	14-01-1999	US WO	5900354 A 9901797 A1	04-05-1999 14-01-1999
US 2002163629	A1	07-11-2002	WO	02091078 A1	14-11-2002
JP 2000085025	A	28-03-2000	NONE		